A HEAVY DUTY CHLORINE-DEPOLARIZED CELL[1]

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ABSTRACT

Chlorine can readily be activated electrochemically at carbon electrodes, these, in combination with conventional metal anodes, giving primary cells of high initial voltage (2.05–2.12 with zinc; 2.85–2.92 with magnesium) and good operating characteristics. Two chlorine-depolarized reserve-type cells are described, one of high capacity at moderate drain (6 amp. per sq. ft. [0.65 amp./dm.^{2}]), the other designed for an exceedingly heavy discharge rate (75–150 amp. per sq. ft. [8–16 amp./dm.^{2}]) for periods of only a few minutes.

INTRODUCTION

The use of atmospheric oxygen as cathodic depolarizer in primary batteries, foreshadowed by the work of Grove (1) in 1839, is now well established in commercial practice (2). Though comparatively little has been done toward the practical utilization of other gases, the literature developed for the fuel cell (3) and to a lesser extent for hydrogen electrodes (4) is evidence of continued interest in gas electrode reactions. There are numerous references (5) to secondary cells in which chloride, bromide, or iodide electrolyte was decomposed during charge, the liberated halogen acting as cathodic depolarizer during discharge, but no great measure of success seems to have been attained through these efforts.

Work initiated in this Laboratory some twenty years ago on gas-depolarized cells (6) included a unit with a chlorine-depolarized carbon cathode and anodes of zinc, aluminum, or magnesium. The heavy duty possibilities of this system were recognized and partially explored but, since suitable applications were lacking at that time, no commercial exploitation was attempted. Nevertheless the project never became completely inactive, and when the need arose for a heavy duty battery, the intensive research and development program was undertaken on which the present report is based.

GENERAL DISCUSSION

Chlorine gas can be utilized electrochemically with comparative ease (7) particularly at electrodes of lampblack, or of the carbon used for air depolarized cathodes, these quickly attaining the theoretical voltage (E_H = 1.358 volt at atmospheric pressure) when exposed to chlorine. Even the relatively inert forms of coke or graphite can be made suitable through the addition of small quantities (<1.0 per cent) of metals such as copper, silver, or platinum. With anode materials, such as magnesium, zinc, or alumi-

[1] Manuscript received June 4, 1948. This paper prepared for delivery before the New York Meeting, October 13 to 16, 1948.

num, cells of high voltage are obtained (cf. Table I) and even with metals lower in the electrode potential series, e.g., iron, fairly satisfactory voltages are possible. Since both anodic and cathodic polarization is comparatively slight, cells can be made capable of operating at drains 20 to 40 times the current densities normally required of primary batteries such as flashlight units.

The cell reaction is simple, e.g.,

$$Zn + Cl_2 = ZnCl_2$$

and, since the chlorides of the anode metals formed are generally extremely soluble, cells of exceptionally high capacity can readily be achieved.

A number of practical limitations militate against the development of a successful chlorine-depolarized cell. Units with liquid electrolyte are entirely feasible, but these involve special problems of construction and may require a waterproofing treatment of the cathode carbon to maintain a high level of depolarizing activity. Such cells are bulky and usually restricted to operation in an upright position. The corrosion of the more anodic metals, e.g., aluminum and magnesium, is normally undesirably high in the

TABLE I. *Operating characteristics of chlorine cells*

Anode material*	Voltage		Duration of test	Excess corrosion
	Open circuit	Discharge, 6 amp./sq.ft. (0.65 amp./sq.dm.)		
			hrs.	%
Zinc (amalgamated)	2.05	1.90–1.60	20	5
Iron	1.45	1.3 –1.15	6	12
Aluminum	2.05	1.75–1.70	10	—
Aluminum (amalgamated)	2.45	2.3 –2.0	7	140
Magnesium	2.85	2.5 –2.4	10	40

* Manganese, for which no service data were obtained, shows an open circuit voltage of 2.25.

presence of free or dissolved chlorine, so that deterioration of a cell during periods of idleness may become excessive. For these and other reasons associated with the specific application for which the chlorine cell was intended, the present report deals only with "dry" reserve-type units, suitable for single continuous discharge, the chlorine being kept separate and introduced only when required.[2]

The early chlorine depolarized cells made in this Laboratory were of the flat-type construction indicated in Fig. 1. The separator layer was ordinarily a cereal paste, e.g., of the $ZnCl_2$: flour type; the cathode comprised a porous matte of carbon black reinforced with paper fiber and moistened with electrolyte, e.g., 5 to 10 per cent $ZnCl_2$ solution. A gas-permeable conducting plate, e.g, carbon, laid directly on the cathode member served to admit chlorine and acted as the external positive electrode. Asphalt applied to the edges made each cell a complete, self-contained unit. A carbonaceous, conducting, impervious coating (9) applied to the external zinc

[2] A different type chlorine-depolarized cell with zinc (magnesium, aluminum) anode, carbon cathode, and chlorine-saturated circulating electrolyte (HCl or seawater-HCl) was developed during World War II in Germany (8).

surface protected the latter from chlorine attack and provided an inert contact with the carbon of the next cell in series. When stacks of cells were used, conducting separator strips were inserted to provide gas distribution channels between the cells. The whole assembly was placed in a suitable container into which chlorine was admitted as required. Operating characteristics of cells discharged at atmospheric pressure on continuous discharge at moderate current drains are shown in Table I.

As shown by the typical discharge curves in Fig. 2, operating voltages are high as compared with those obtained with air depolarization, and well sustained over considerable periods of time. Corrosion of magnesium and particularly of amalgamated aluminum anodes is great, but not prohibitively so for cells designed for a single discharge of short duration.

The more recent cells were developed to meet a demand for batteries capable of delivering very heavy current at well-sustained voltages for comparatively brief periods, e.g., five to ten minutes. The high voltages in-

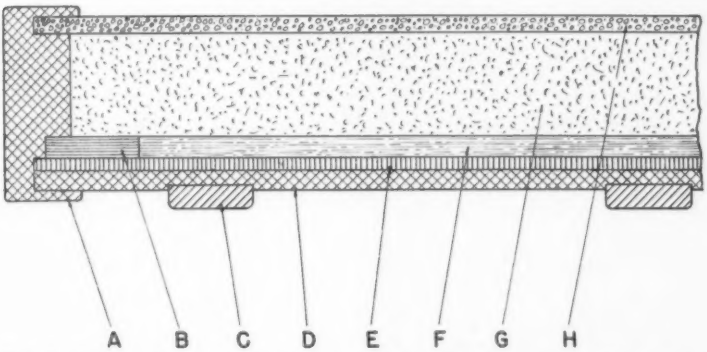

FIG. 1. Construction of early chlorine depolarized cell. A—asphaltic outer seal, B—paste retaining member, C—carbon spacer strips, D—gas impervious, conducting coating, E—anode, F—paste layer, G—carbon cathode, H—gas-permeable carbon terminal electrode.

volved required stacks of many cells in series; and, since minimum volume was a primary requisite, separate spacers had to be eliminated and provision made for access of chlorine through a carbon diffuser layer. A suitable cell construction, shown in Fig. 3, comprised a porous coke or graphite diffuser, making contact at the top with the carbon-coated zinc surface of the adjacent cell and at the bottom with a molded layer of electrolyte-moistened carbon black layer, the latter forming the active cathode element. The paste of either cereal or methyl cellulose type was held in a cotton netting spacer to prevent collapse or lateral displacement under pressure. The insertion of a cellophane film, as shown, between paste and cathode made it possible to use very thin paste layers, e.g., 0.010 inch, without danger from internal short circuits. With this construction, the thickness of a complete cell could be kept down to about 0.125 inch (0.318 cm.) even in the largest units built in the course of this work.

Much of the preliminary work was done with cells of approximately six

square inches (39 cm.²) of active surface, operated at about 0.85 ampere per square inch (13.2 amp./dm.²). As the work progressed, larger cells were developed, most of the subsequent data in this report representing operation of units 185 square inches (11.6 dm.²) in area, at currents of 158 amperes or better.

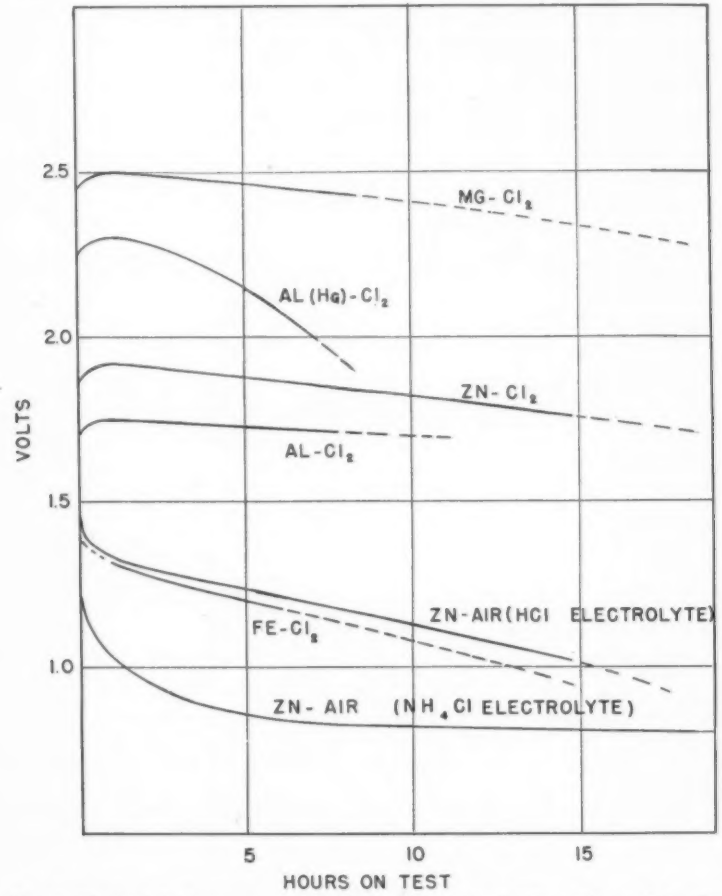

FIG. 2. Typical discharge curves of chlorine depolarized cells. (Current density—0.042 ampere per square inch [0.65 amp./dm.²]).

Finished batteries, kept in air-tight metal containers in oxygen-free atmosphere or partial vacuum, suffered little deterioration in storage for periods of eight to ten months. Activation was accomplished in the laboratory by evacuation of the containers to about 0.05–0.1 atmosphere, followed by admission of chlorine, in the form of gas for small units, and as

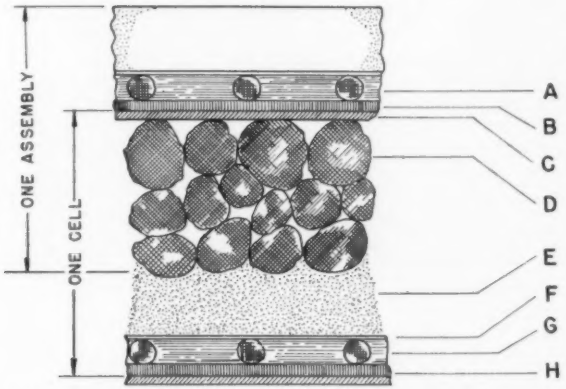

FIG. 3. Construction of chlorine depolarized battery. A—paste layer with netting reinforcement, B—anode, C—inert, non-porous impervious conducting coating, D—diffuser element of porous carbon particles, E—carbon cathode, F—cellophane, G—paste layer, H—anode.

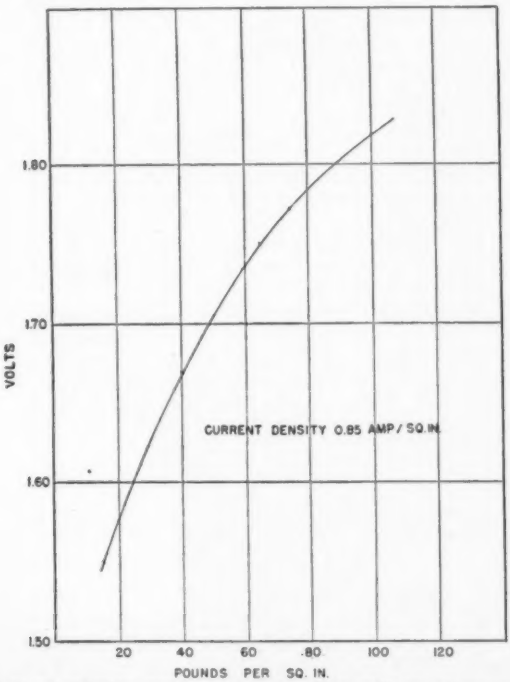

FIG. 4. Effect of chlorine pressure on operating voltage at room temperature (Current density—122 amperes per square foot [13.2 amp./dm.^{2}]).

liquid for the full sized cells. In both instances the final chlorine pressure was at or near the equilibrium value, i.e., 5–7 atmospheres at room temperature when activation was completed.

The effect of pressure on the open circuit voltage of the cell is small, amounting theoretically (10) to a rise of only 0.025 volt for the change from

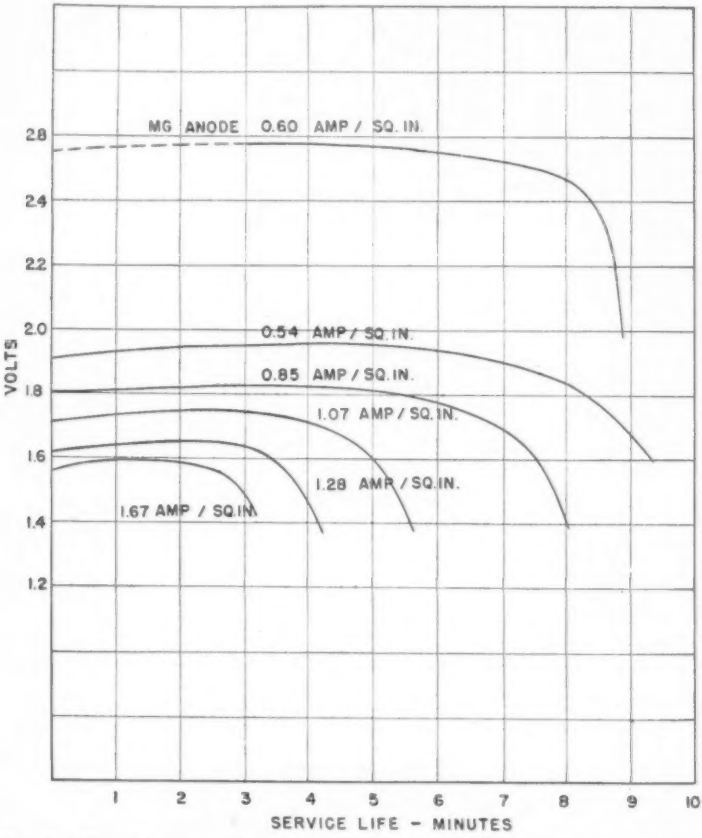

FIG. 5. Effect of current density on operation of chlorine depolarized cells with zinc anodes. (Mg anode cell at 0.60 amp./sq. in. [9.3 amp./dm.^{2}] inserted for comparison).

one to seven atmospheres. On the other hand, its effect on operating voltage, as shown in Fig. 4, is very great, because of the increased concentration and, therefore, the continued availability of chlorine at the active cathode surface. As is to be expected, the operating voltage level reaches a limiting value as the equilibrium pressure of chlorine is approached. Current densities obtainable at equilibrium pressures with cells of this type

were exceedingly high,[3] most of the evaluation work being done at 0.85 ampere per square inch (13.2 amp./dm.^{2}), and as much as 1.67 amperes per square inch (26 amp./dm.^{2}) being realized experimentally.

Typical discharge curves (obtained on 18-cell batteries employing zinc anodes) are shown in Fig. 5. The initial rise in operating voltage was probably due primarily to temperature effects caused by attack of free chlorine on cell components. Capacity was limited largely by the quantity of electrolyte and, therefore, by the volume or, more specifically in this case, by the thickness of the cell. There was no serious polarization, either anodic or cathodic, and the ampere-hour capacity at useful voltage was, therefore, not greatly affected by current density in the range shown in Fig. 5.

Initial closed circuit voltage fluctuated about 0.1 volt in the temperature range of +7 to 35°C., not enough to interfere with satisfactory performance under normal operating conditions. Although lowering of temperature increases sorption and solubility of gases, it is the chlorine electrode that suffers most in the present instance, presumably because of the possible formation, below 28°C., of chlorine hydrate ($Cl_2 \cdot 6H_2O$), relatively insoluble and probably of reduced depolarizing activity.

Cells made with magnesium anodes were found to be somewhat less stable during storage than the corresponding zinc units; they were not capable of quite as high current density; their capacity was not as great, owing to the lower solubility of the chloride and the fact that the latter abstracts larger quantities of water from the electrolyte when it crystallizes (as $MgCl_2 \cdot 6H_2O$) from saturated solution. Nevertheless they were capable of satisfactory service, their high operating voltage (2.25–2.4 at normal load, e.g., 0.85 ampere per square inch [13 amp./dm.^{2}]) constituting an important advantage over the corresponding zinc element.

ACKNOWLEDGMENT

The authors take this opportunity to acknowledge their indebtedness to Bureau of Ordnance, Navy Department, for permission to publish certain portions of this paper, and also to members of the National Carbon Co., Inc., Research Laboratory staff, particularly to M. R. Hatfield, H. M. Zimmerman, and R. P. Fox for some of the measurements used.

Any discussion of this paper will appear in the discussion section of Volume 94 of the Transactions of the Society.

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[3] Some measure of the magnitude of such current densities in dry type cells may be obtained from the fact that a conventional D-size dry cell, operating with an ordinary flashlight bulb, delivers only about 0.04 ampere per square inch (0.062 amp./dm.^{2}).

LEAD REFINING WITH SULFAMATE BATHS[1]

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ABSTRACT

The plant of an Italian firm for electrolytic lead refining with sulfamate baths, A. Tonolli & Co., is briefly described.

INTRODUCTION

The use of the sulfamate baths in plating and electrometallurgy has been introduced by L. Cambi and R. Piontelli (1), by R. Piontelli and A. Guilotto (2) (for Pb, Ag, Ni, Co, Fe, Cu, Zn, Cd, Rh, etc.), and by the independent researches (concerning Pb only) of Mathers and Forney (3).

Before the war, a pilot plant for crude lead refining with sulfamate baths was set up by the author in the factory of the Italian firm for refining of nonferrous metals, A. Tonolli & Co., near Milan. Parallel experiments were undertaken in analogous conditions with the Betts method.

After a long series of fully satisfactory runs in the pilot plant, industrial plants for the lead refining in sulfamate bath and for the preparation of the sulfamic acid were designed and built after the war with the cooperation of the technical staff of A. Tonolli & Co.

DESCRIPTION OF THE PLANT

The present plant has a daily production capacity of about 9 metric tons, which before the end of the year will increase to 18 metric tons.

The cells are of the usual multiple system, arranged in cascades of 9. They are made of appropriately lined wood and have a working capacity of about 1 cubic meter.

The anodes (14 in each cell) are of secondary lead from various sources (mean analysis: Pb 95 per cent; principal impurities: Sb, Cu, Bi, Sn, Ag), and are cast in the usual form. The starting cathode sheets are made by casting refined lead in plates.

The electrolyte contains about 80 g./l. Pb, 100 g./l. free H_3NSO_3H, and a proper amount of an especially selected addition agent.

The cathodic current density is 120–100 amp./sq.m., the lower value being adopted when the anodes contain the highest amount of impurities. The mean current efficiency (data for one year) is about 96 per cent. The cathode life is 6 to 7 days.

The mean cell voltage is about 0.5 volt at 30°C. with particularly impure anodes; after 8 to 10 days it is as high as 0.65 volt. The mean power consumption in the cells is, therefore, about 0.135 kw.-hr./kg. of lead produced.

The most impure anodes require particular care for avoiding electrolyte (and dissolved lead) losses in the anode slimes, and require expedients for avoiding some enrichment of impurities in the electrolyte.

The produced lead tests 99.992 per cent (mean of ten analyses).

[1] Manuscript received June 4, 1948. This paper prepared for delivery before the New York Meeting, October 13 to 16, 1948.

After about one year of industrial service, the plant has demonstrated the exceedingly good qualities of the sulfamate baths for lead refining.

The general advantages of this electrolyte have been illustrated (2, 3, and 4). The principal advantages relate to: the high solubility of the acid and of its salts; the strong reactivity and low toxicity of the acid; and the fact

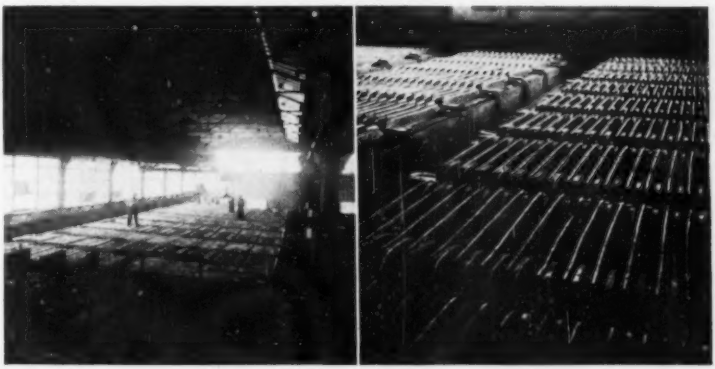

FIG. 1. Views of the plant

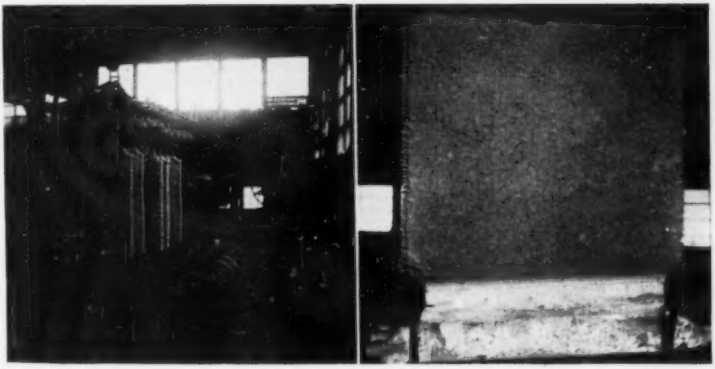

FIG. 2. Cathodes. At left, extraction (half cell); at right, after 6 days life

that the acid is not hygroscopic, but solid, easy to handle and store. The bath preparation is easy and the baths are very stable.

There are three particular advantages. First, the tin content of the anodes, which pass entirely into the cathodes in the Betts electrolysis, is harmless until over 1 per cent (especially in the presence of high antimony contents which may indicate the formation of intermetallic compounds). In addition, bismuth, copper, silver, and arsenic give no trouble. Second,

the attack of the very impure anodes is more regular than in the Betts process because the fluosilicates are more easily hydrolized then the sulfamates in the slime blankets where they attain very high concentrations. Third, the electrolyte losses in the anode slimes are less significant than in the Betts process.

ACKNOWLEDGMENT

The author wishes to thank Mr. L. Tonolli, General Director, and the technical staff of A. Tonolli & Co. for the helpful cooperation and for the permission to publish these data.

Any discussion of this paper will appear in the discussion section of Volume 94 of the Transactions of the Society.

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ELECTROWINNING OF MANGANESE FROM CHLORIDE ELECTROLYTES[1]

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ABSTRACT

A study was made to determine the possibility of continuous electrowinning of manganese using chloride electrolytes. The principal variables of the process were investigated, namely: current density, solution concentrations, pH, temperature, time of deposition, and other optimum conditions. It was concluded that the electrowinning of manganese from a chloride electrolyte is feasible. A comparison between the chloride process and the sulfate process is made pointing out the chief advantages and disadvantages.

INTRODUCTION

Research and development work on a process for the electrowinning of manganese from low-grade ores has been carried on by the Bureau of Mines for the past 12 years. A process has been developed for electrowinning of manganese, using sulfate electrolyte, and has been extensively reported in the literature (1–8). In late 1946, research was begun at the Bureau of Mines Electrometallurgical Laboratory at Boulder City, Nevada, to determine the possibility of electrowinning manganese on a continuous basis from chloride electrolytes.

[1] Manuscript received June 4, 1948. This paper prepared for presentation before the New York Meeting, October 13 to 16, 1948.

Very little attention has been directed toward cathodic deposition of manganese from chloride electrolytes as evidenced by the scarcity of publications in the literature. Oaks and Bradt (9) extensively investigated deposition from chloride electrolytes using soluble, 96 per cent Mn anodes or insoluble platinum anodes. They reported the optimum conditions for obtaining a good quality deposit to be as shown in Table I.

Oaks and Bradt's investigations were carried out on a very small scale and in no case was more than 1 g. of manganese obtained. They concluded that the manganese chloride electrolyte was not, at that time, capable of continuous use because the anode efficiency was greater than the cathode efficiency, resulting in gradual increase of manganese concentration in the solution and the subsequent formation of $Mn(OH)_2$. No data on hydrogen ion concentrations were reported.

Thanheiser and Hubold (10) obtained good deposits at 10 amp./dm.^{2} current density from an electrolyte containing 47 to 82 g./l. Mn as the chloride and 160 g./l. NH_4Cl. They found that the pH of the electrolyte decreased during electrolysis, and it was necessary to make continuous additions of ammonia in order to maintain the pH in the desired range. They

TABLE I. *Optimum conditions for electrolysis reported by Oaks and Bradt*

Anode	Commercial (96% pure) manganese
Cathode	Cleaned and buffed copper sheet
Cell	Porous diaphragm
Electrolyte	300 to 400 g./l. $MnCl_2$ and 30 g./l. NH_4Cl
Current density	20 amp./dm.^{2}
Voltage	4.5 to 5.5 volts
Stirring of catholyte	"Quite vigorous"
Temperature	26° C.

had difficulty, however, in obtaining reproducible results because of deterioration of the electrolyte.

GENERAL PLAN OF WORK

Experience with the electrolysis of manganese from sulfate electrolyte has shown that a number of interdependent variables have an important effect on manganese deposition. It appeared likely that a large number of tests would be required to obtain the necessary data. To accumulate enough data in a reasonable time the work was divided into two parts. First, the effect of catholyte composition, temperature, and current density was studied in a series of tests of short duration in small cells; variations in solution composition were minimized by feeding fresh solution to the cells rapidly. Second, larger cells were placed in continuous operation to obtain information not obtainable in the first series of tests, namely, to determine the conditions that could be obtained continuously in an operating cell, and to determine the effects of feed rate and time of deposition.

EXPERIMENTAL

All solutions used in this investigation were prepared in a manner similar to that used for sulfate solution electrolysis. Ore from Three Kids Mine,

Clark County, Nevada, containing 20 to 25 per cent Mn was used as the source of manganese. The ore was given a reducing roast to reduce the MnO_2 to MnO which is acid-soluble. The reduced ore was leached with spent electrolyte from the cells containing HCl, NH_4Cl, and $MnCl_2$, and the residue filtered and discarded. Impurities, such as copper, arsenic, zinc, and small amounts of nickel, were precipitated by H_2S at a pH of 6.5 to 6.8. After filtering, a small amount of $FeCl_3$ or $FeSO_4$ was added and the solution aerated until all the iron was precipitated as ferric hydroxide. After filtering again, this solution was used for electrolysis.

Small cell tests

The small cells used in the first series of tests were rectangular, made of Lucite, and had a capacity of 220 ml. Each contained one cathode, 1-in. (25-mm.) wide with 2-in. (51-mm.) immersion, and two graphite anodes of similar size. Cathode and anodes were separated by porous No. 1 Vinyon diaphragms to form two anolyte and one catholyte compartments. The anolyte compartments were interconnected to insure uniformity. Four cells and a copper coulometer were connected in series in each test. From 2 to $2\frac{1}{2}$ l. of solution were fed to each cell during a single run of 2 to 3 hours duration. This rate of flow was rapid enough so that the manganese content of the catholyte was not more than one gram per liter lower than that of the feed solution. The pH of the catholyte did not differ from that of the feed by more than 0.2 except in a few cases when the solution was poorly buffered. The catholyte concentration was thus kept nearly constant in each test. In reporting the results, the final composition of the catholyte was considered to represent the average composition throughout the electrolysis period.

In electrolysis of manganese sulfate solutions, addition of a small amount of SO_2 is necessary for continuous deposition of manganese. Fig. 1 shows the effect of adding various amounts of SO_2 to an electrolyte containing 140 g./l. NH_4Cl and 15 g./l. Mn in the form of $MnCl_2$. The results indicate that the presence of at least 0.05 g./l. SO_2 is necessary for maximum current efficiency. The exact function of the SO_2 has not been determined. One of its functions, however, is to prevent oxidation of the catholyte and consequent precipitation of tetravalent manganese. That this is not the sole function of SO_2 is shown by the second curve in Fig. 1. Hydroxylamine, when substituted for SO_2, was extremely effective in preventing oxidation but current efficiencies were consistently poor. Table II shows the affect of other sulfur compounds on the current efficiency of manganese electrodeposition.

Fig. 2 shows the effect of varying pH on current efficiency at four different manganese concentrations. All other conditions were held constant. For each metal concentration there is a pH at which the current efficiency is a maximum. This maximum will be termed the "critical pH" in this discussion. In Fig. 3 the same data are plotted differently to emphasize the effect of manganese concentration on critical pH.

Consideration will show that the concept of a critical pH is of value in the continuous deposition of manganese. If the pH of the catholyte increases to a value much greater than the critical pH there is an appreciable decrease in current efficiency. A decrease in current efficiency results in the for-

mation of more base in the catholyte and a further increase in pH. Furthermore, unless the rate of feed of fresh solution to the cell is decreased immediately, the lower current efficiency results in a higher manganese concentration in the catholyte which in turn lowers the critical pH. The deposit becomes dark and contaminated with oxide; eventually manganese hydroxide precipitates in the cell, the deposit turns black, and deposition practically ceases. The critical pH thus defines a practical upper limit of

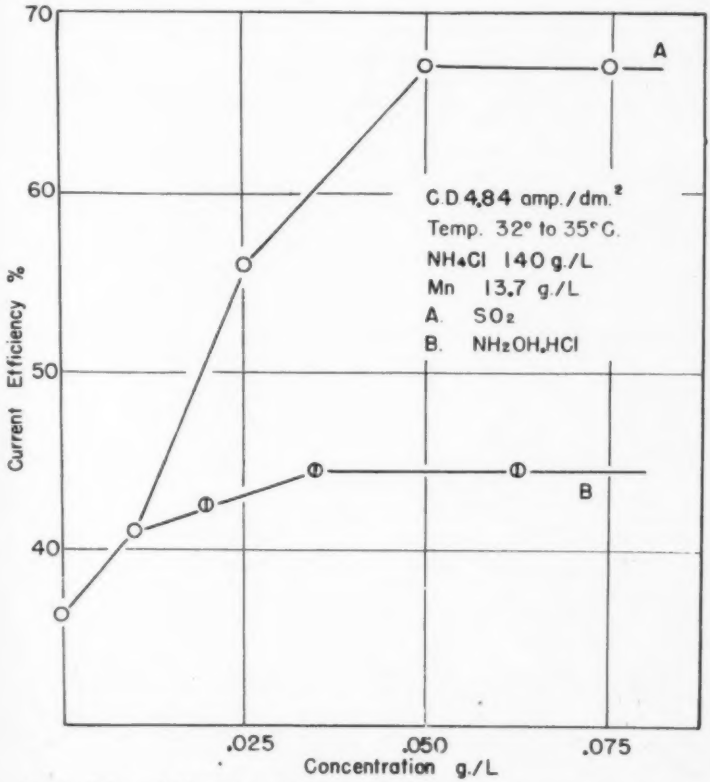

FIG. 1. Effect of SO_2 and $NH_2OH \cdot HCl$ concentrations on current efficiency

pH for continuous cell operation. Deposition is possible below the critical pH at decreased current efficiency.

In practice, the lower limit of pH is determined by the buffering characteristics of the solution; below 6.5, the pH may drop very rapidly until deposition is impossible.

The data obtained from deposition tests with varying NH_4Cl concentration are shown in Fig. 4, 5, and 6. The current efficiency decreases slightly

as the NH_4Cl content is increased. The critical pH is raised by increasing NH_4Cl and lowered by decreasing NH_4Cl, but the effect is less marked than that of metal content. Curves B and C in Fig. 4 and 5 illustrate the beneficial effect of decreasing the manganese content when the NH_4Cl concentration is low and increasing the manganese concentration as the NH_4Cl content is increased. The NH_4Cl content of the bath serves a triple purpose: increasing the electrolyte conductivity, preventing the precipitation of manganese, and buffering the catholyte pH. As the NH_4Cl concentration is decreased, conditions in the cell are more erratic and reproducible results are more and more difficult to obtain. The lower limit of NH_4Cl content is best determined by continuous operation of larger cells.

Fig. 7 shows the result of tests at 22, 45, and 90 amp./sq. ft. (2.37, 4.85, and 9.68 amp./dm.^{2}) from solution containing 140 g./l. NH_4Cl and 13 to 14

TABLE II. *Effect of sulfur compounds on deposition*

Addition agent	Concentration	Current efficiency
	g./l.	%
None	0	10.6
$Na_2S_2O_3$	0.01	21
$Na_2S_2O_3$	0.025	61
$Na_2S_2O_3$	0.05	72
$Na_2S_2O_3$	0.10	71
$Na_2S_2O_3$	0.12	58
$Na_2S_2O_3$	0.20	63
$Na_2S_2O_3$	0.25	48
$Na_2S_2O_3$	0.40	28
None	0	14
KCNS	0.025	58
KCNS	0.125	68
KCNS	0.24	69
p-toluene sulfonic acid	0.5	4
sulfanilic acid	0.25	3
sodium sulfo carbolate	0.25	3
1 amino-8-naphthol-3-6 disulfonic acid	0.25	5
p-amino benzene sulfonic acid	0.25	2
2-napthylamine 6-8 disulfonic acid	0.25	2
1-napthylamine 3-6-8 trisulfonic acid	0.25	18

g./l. Mn at varying pH. The results of these 2-hour tests indicate that current efficiency increases with increasing current density. It must be stressed, however, that these are short-time runs. If the electrolysis had been continued for 24 hours or more, the growth of nodules and trees would change the results markedly.

From the tests shown so far on the interrelationship of solution pH, salt concentrations, and current density, the following generalizations may be made.

1. As the SO_2 concentration of the catholyte is increased up to 0.05 g./l., the current efficiency is increased. Above 0.05 g./l., there is no further beneficial effect of SO_2 on current efficiency.

2. When the NH_4Cl content and current density are constant, the catholyte manganese content and pH can be varied simultaneously to give the same current efficiency. As the manganese content is increased, the pH

must be decreased to maintain maximum efficiency. For any given manganese concentration, there is a critical pH at which the maximum current efficiency is obtained, and this critical pH decreases with increasing manganese.

3. When the manganese and NH_4Cl contents are constant, the critical pH is decreased slightly by increasing current density. The control of

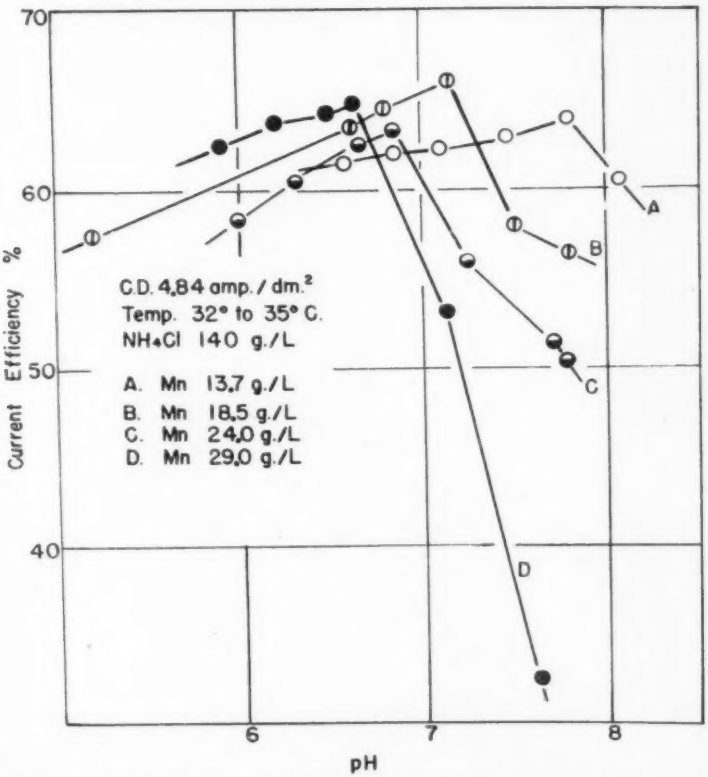

FIG. 2. Effect of pH on current efficiency, manganese concentration variable

solution pH is more critical at low current densities than at high current densities.

4. Increasing NH_4Cl content raises the critical pH.

5. For maximum current efficiency, the manganese content should be lowered as the NH_4Cl decreases in the range 200 g./l. to 110 g./l.

Large-cell tests

With the results of the small-cell tests as a guide, a series of tests were made with larger cells for longer periods of time. The cells used had a

capacity of 10 l. and were constructed of a laminated phenolic resin. They contained 1 stainless steel cathode 4.5 in. (114 mm.) wide, immersed 8 in. (203 mm.), and 2 graphite anodes. The 2 anode compartments were formed by suspending diaphragm-covered frames, 1½ in. (38 mm.) wide by 5

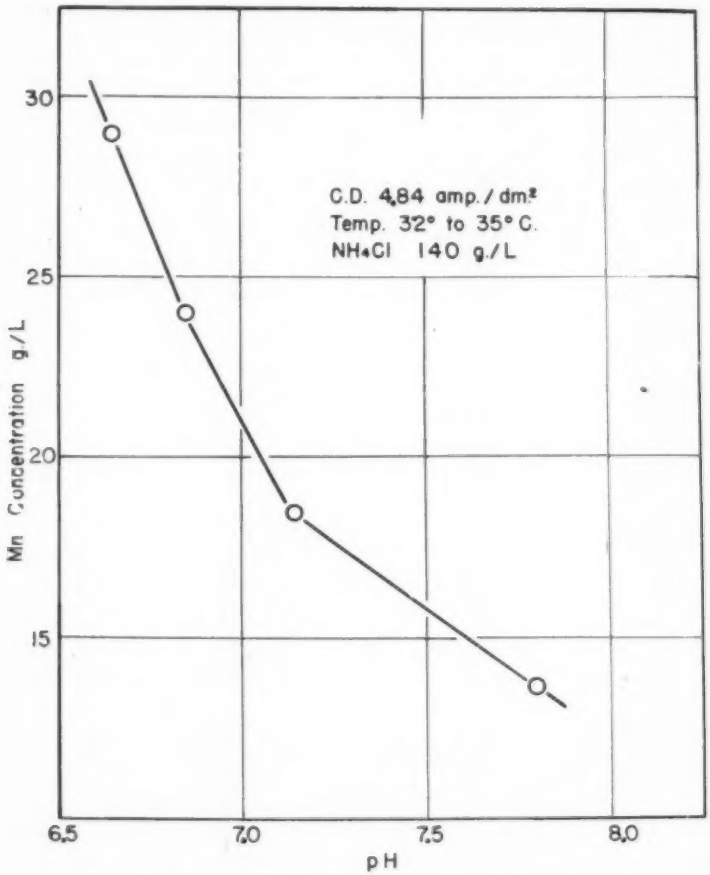

FIG. 3. Effect of manganese concentration on "critical" pH

in. (127 mm.) long by 10 in. (254 mm.) deep, in the cell. Each anode compartment had a discharge tube extending through the side of the cell at the desired height. In this manner, the main body of the solution was catholyte, and the solution inside each anode frame was the anolyte. New solution was fed to the catholyte at the desired rate, and anolyte discharged

automatically at the same rate through the tube leading from each anode compartment through the side of the cell. Canvas diaphragms were badly attacked by the electrolyte. No. 1 Vinyon made a satisfactory diaphragm and was used throughout the investigation. All the pH determinations were made with a Beckman pH meter Model G.

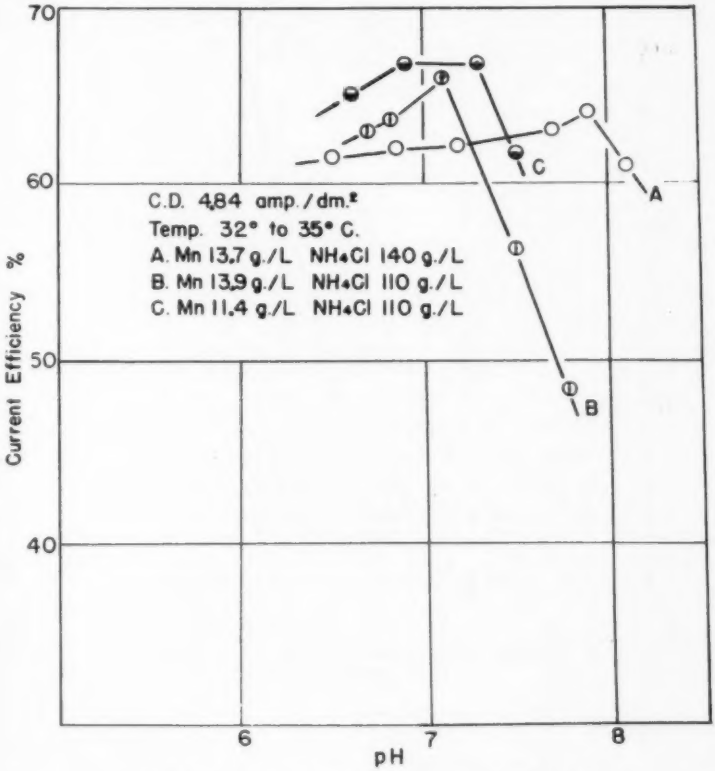

FIG. 4. Effect of pH on current efficiency, Mn and NH_4Cl concentration variable

Two of these cells were placed in continuous operation to determine what conditions could be obtained in an operating cell and to study the effects of solution flow rate and time of deposition. Tests were first made with NH_4Cl content varied from 75 to 110 g./l. and it was found that below 100 g./l., the catholyte pH was difficult to maintain at 7.0 or above with consequent loss in current efficiency. An NH_4Cl content of 100 to 110 g./l. was then adopted as standard for future work.

The rate of solution flow through the cell determines the quantity of manganese removed from the solution. The difference in manganese concen-

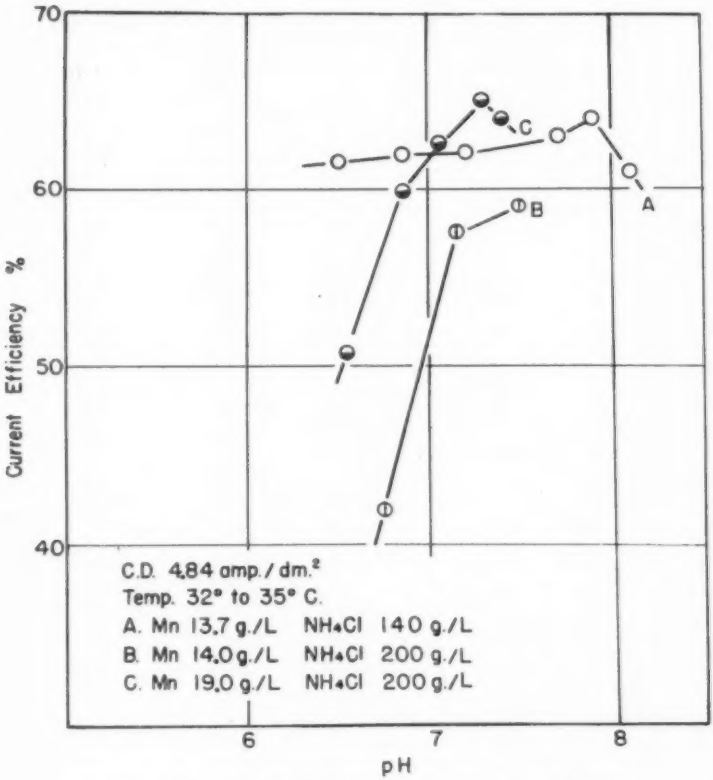

FIG. 5. Effect of pH on current efficiency, Mn and NH_4Cl concentration variable

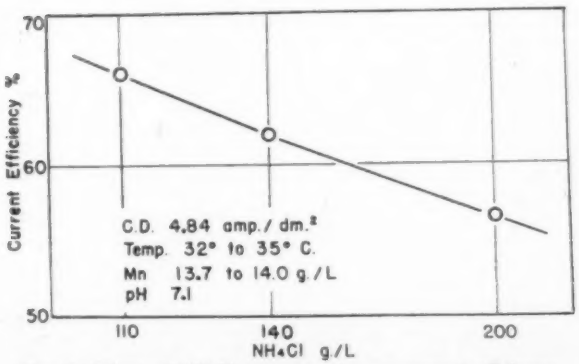

FIG. 6. Effect of NH_4Cl concentration on current efficiency

tration between the feed solution and cell catholyte will be called the "solution strip" in this paper. It is desirable to operate with the largest solution strip possible, because this lessens the amount of solution necessary to be processed. The principal effect of the rate of solution flow is on the catholyte pH. As the solution strip is increased with a consequent decrease in solution flow, the catholyte pH decreases and cell control becomes critical. Numerous runs were made varying the solution strip from 20 to 60 g./l.

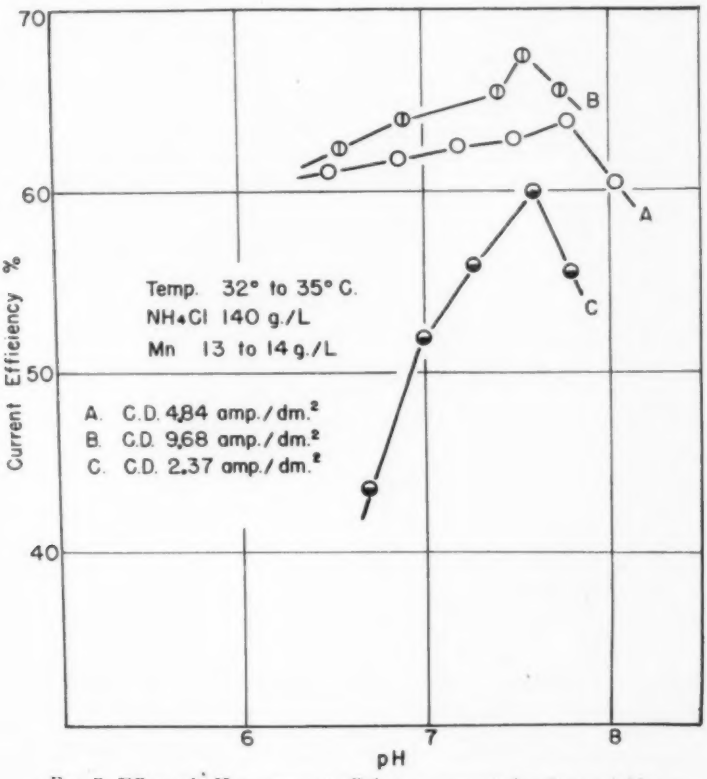

FIG. 7. Effect of pH on current efficiency, current density variable

It was found impossible to maintain the cell pH above 6.0 when stripping more than 45 g./l. When the solution strip was 20 to 40 g./l., the pH remained in the range 7.0 to 7.4 with resultant current efficiency of 66 to 70 per cent. A solution strip of 40 g./l. was adopted as the most desirable for continuous electrolysis.

The operating temperature of a cell should be as high as possible to minimize electrolyte cooling. Several continuous runs showed that the cells could be operated as high as 40°C. without undue adverse effect on the roughness of the deposit or current efficiency.

Time of deposition and current density were investigated simultaneously by operating the cells for varying periods of time at 34 amp./sq. ft. (3.66 amp./dm.^{2}), 45 amp./sq. ft. (4.84 amp./dm.^{2}), and 56 amp./sq. ft. (6.02 amp./dm.^{2}). It was found that a cathode containing the manganese deposit could be withdrawn from the cell at any time, dipped in dilute sodium or potassium dichromate, washed, dried, weighed, and returned to the cell for further electrolysis without any loss of current efficiency. Therefore, the cells were operated in this manner to determine the current efficiency at desired intervals of time. The results are shown in Table III.

The deposit obtained at 56 amp./sq. ft. (6.02 amp./dm.^{2}) became very treed and nodular after 40 hours and would not be suitable for use. The 96 hour deposit at 45 amp./sq. ft. (4.84 amp./dm.^{2}) was $\frac{3}{16}$ inch (4.75 mm.) thick and, though nodular, it was dense and compact. If this deposit could

TABLE III. *Effect of time of deposition at different current densities*

Cumulative time	Current efficiency		
	56 amp./sq.ft.[3] (6.02 amp./dm.[2])	45 amp./sq.ft.[3] (4.84 amp./dm.[2])	34 amp./sq.ft.[3] (3.66 amp./dm.[2])
hrs.	%	%	%
8	—	75.8	—
16	70.7	75.2	—
24	68.6	74.9	71.3
32	65.7	74.4	—
40	64.8	74.0	—
48	—	73.5	70.8
56	—	73.2	—
64	—	72.9	—
72	—	72.5	70.1
80	—	71.8	—
88	—	71.3	—
96	—	70.4	68.6
130	—	—	67.5
144	—	—	66.5
165	—	—	65.2

Feed solution: Mn—53 g./l., NH_4Cl—100 g./l.
Catholyte: Mn—14 g./l., SO_2—0.05 to 0.10 g./l.
pH—7.2 to 7.4, Temp.—37 to 39°C.

be duplicated in a large commercial cell, at least 5 to 6 lb. (2.3 to 2.7 kg.) of manganese per sq. ft. (250 to 300 g./dm.^{2}) of cathode can be obtained with a resultant saving of labor for cathode stripping and preparation. The deposit obtained at 34 amp./sq. ft. (3.66 amp./dm.^{2}), although less rough than the 45 amp./sq. ft. (4.84 amp./dm.^{2}) deposit, would be less desirable because of the lower current efficiency.

The voltages of the large cells used for continuous electrolysis of chloride electrolytes are much lower than those required for sulfate electrolysis. The cell voltages on the tests shown in Table III were as follows:

Current density	*Cell voltage*
56 amp./sq. ft. (6.02 amp./dm.^{2})	3.60
45 amp./sq. ft. (4.84 amp./dm.^{2})	3.44
34 amp./sq. ft. (3.66 amp./dm.^{2})	3.24

A comparable cell operating with sulfate electrolyte at 45 amp./sq. ft. (4.84 amp./dm.²) current density would require 4.8 volts. This difference is due mainly to the higher electrical conductivity of the chloride electrolyte, and a comparison of cell-voltage components is shown in Table IV.

The electrode potentials shown in the table were measured with a calomel half-cell and a glass probe. Solution was kept flowing through the probe tip while a measurement was being made to prevent gas bubbles from entering the tip.

Anode reactions

Graphite was chosen as the most logical anode material because of its stability in chloride electrolytes and all tests reported were made using graphite anodes ½ in. (13 mm.) thick. No MnO_2 was deposited at the anode as at lead alloy anodes in sulfate electrolytes. A small amount of chlorine, however, was evolved at the anodes to cause discomfort to the cell operators, so it was necessary to place a small hood over each cell to remove the fume.

TABLE IV. *Comparision of sulfate and chloride cell potentials*

	Potential at 50 amp./sq.ft. (5.38 amp./dm.²)	
	Sulfate cell	Chloride cell
	volts	*volts*
Cathode to solution	1.33	1.29
Catholyte IR drop, 1 in. (25 mm.) of solution	0.95	0.27
Diaphragm	0.03	0.05
Anolyte IR drop, ¾ in. (19 mm.) of solution	0.52	0.14
Anode to solution	2.0	1.82
Total	4.83	3.57

Franz Jirsa (11) studied the anode reactions in the electrolysis of NH_4Cl solutions but no references were found to NH_4Cl and $MnCl_2$ solutions. He found that the liberated chlorine could react with the ammonium salts to form various chloramines depending on the cell conditions.

Analysis of the anolyte always shows the disappearance of ammonium chloride and the formation of more HCl than is required to dissolve the deposited metal, the excess HCl being equivalent to the apparent loss of NH_4Cl.

Samples of the gas evolved at the anode were collected and analyzed with the following results:

Current density	40 amp./sq. ft. (4.3 amp./dm.²)
Temperature	35°C.
Composition of anolyte:	
Mn	14 g./l.
NH_4Cl	115
HCl	35
Composition of gas:	
N_2	99% by volume
Cl_2	0.8 to 1%

The reaction products can be accounted for by an assumption that the anode reaction is essentially an oxidation of ammonia to nitrogen:

$$6\ Cl^- = 3\ Cl_2 + 6e \qquad (1)$$

$$2\ NH_4Cl + 3\ Cl_2 = N_2 + 8HCl \qquad (2)$$

Reaction 2 represents the final result, but probably not the actual mechanism of the reaction. Intermediate products are evidently formed; evolution of gas from the anolyte continues for some time after it leaves the cell. During cell operation, the anolyte frequently becomes dark in color indicating the presence of small amounts of $MnCl_3$ or $MnCl_4$. These are unstable and the anolyte decolorizes on standing.

TABLE V. *Analysis of manganese metal*

Element	Per cent
Fe	0.0035
Cu	0.001
Total S	0.018
Sulfide S	0.016
Pb	0.001
As	0.0005

TABLE VI. *Optimum electrodeposition conditions*

Anode	Graphite
Cathode	Stainless steel
Diaphragm	Vinyon
Feed solution, Mn	54 g./l.
NH_4Cl	110 g./l.
Catholyte, Mn	14 g./l.
SO_2	0.05 to 0.10 g./l.
Current density	45 amp./sq. ft. (4.84 amp./dm.^{2})
Time of deposition	72 hr.
Cell potential	3.4 volts
Current efficiency	70%

Time did not permit further detailed examination of the anode reactions but it is recommended as a subject worthy of future study.

Analysis of manganese deposits

A typical analysis of the manganese metal obtained is shown in Table V. The principal impurity is sulfur which is due to the added SO_2. The purity of the manganese is in excess of 99.9 per cent.

SUMMARY AND CONCLUSIONS

Results of experiments on the electrodeposition of manganese from chloride solutions have been presented and, from the data obtained, it is concluded that continuous electrowinning of manganese is definitely possible. The optimum electrodeposition conditions, based on the data presented, are shown in Table VI.

In comparing the processes using chloride or sulfate electrolytes, the following advantages of the chloride process are apparent:

1. Lower cell voltage reduces power consumption about 25 per cent.
2. A greater manganese recovery from the feed solution is obtained, therefore, the solution-preparation plant need be only about one-half as large as for the sulfate-electrolyte process.
3. Longer time of deposition reduces the amount of labor for cathode handling.
4. No MnO_2 is deposited at the anode.

However, the chloride process has certain disadvantages, namely:

1. The solutions are more corrosive, requiring expensive materials of construction.
2. The loss of nitrogen at the anode must be replaced by NH_3.
3. Ventilation of cells is necessary to remove obnoxious fumes produced at the anodes. Before an economic comparison of the two processes can be made, it will be necessary to operate the chloride process on a continuous cyclic pilot-plant scale.

ACKNOWLEDGMENT

The authors wish to acknowledge a debt of gratitude to C. W. Davis, Chief, Boulder City Branch, Metallurgical Division, Bureau of Mines, under whose general supervision the work was carried on, and to T. E. Hill, Jr., E. C. Perkins, metallurgists, and William Curry, technologist, who performed most of the laboratory work.

Any discussion of this paper will appear in Volume 94 of the Transactions of the Society.

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PILOT-PLANT PRODUCTION OF ELECTROLYTIC CHROMIUM[1]

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ABSTRACT

The operation of a pilot plant for the production of electrolytic chromium from low-grade domestic ores is discussed, with emphasis on the techniques necessary to produce an adequately pure chromic sulfate electrolyte from the mixture of metal sulfates obtained by acid dissolution of the ore. Equipment flowsheets are included with a discussion of the materials of construction. Since publication of the original paper, improvements have been made in the electrodeposition step to increase the current efficiency and decrease the impurities in the metal. Typical operating data are tabulated for each operation.

INTRODUCTION

The Bureau of Mines has carried on research and development work for many years on the economic utilization of the substandard chromium ores from the Western States. One phase of this program is the electrowinning of pure chromium from the more abundant ores or their concentrates.

A previous report (1) discussed the laboratory work, the preliminary pilot-plant development of the process, and the effect on the electrodeposition step of the most troublesome impurities. The present report is a discussion of the data obtained by continuous operation of the pilot plant, with emphasis on the removal of impurities from the electrolyte and the solution of construction problems. The pilot plant has produced about 10,000 lb. (4,500 kg.) of metal, starting at 50 lb./day (22.7 kg.) and building up to 70 lb. (31.8 kg.).

Work is continuing further to decrease the cost of the process and bring it into commercial application. To meet the objective of utilizing domestic ores, metal produced by this process must be competitive with low-carbon ferrochrome.

EXPERIMENTAL

Equipment

The pilot plant is housed in a corrugated galvanized steel building, 50 ft. by 60 ft. (15 m. x 18 m.). One corner, enclosed in a dust-tight room, serves as a tank house. The digester, aging thickeners, various storage tanks, and boiler are located outside the main building. All grinding is performed in a general mill building which has a much larger capacity than the chromium pilot plant, and the filter cake is trucked to the pilot plant. A general flow sheet is shown in Fig. 1.

Chromite ore or gravity concentrate, whichever is used for plant feed, is wet-ground in lots of 10 to 25 tons to pass a 325-mesh screen, using a ball

[1] Manuscript received June 4, 1948. This paper prepared for delivery before the New York Meeting, October 13 to 16, 1948.

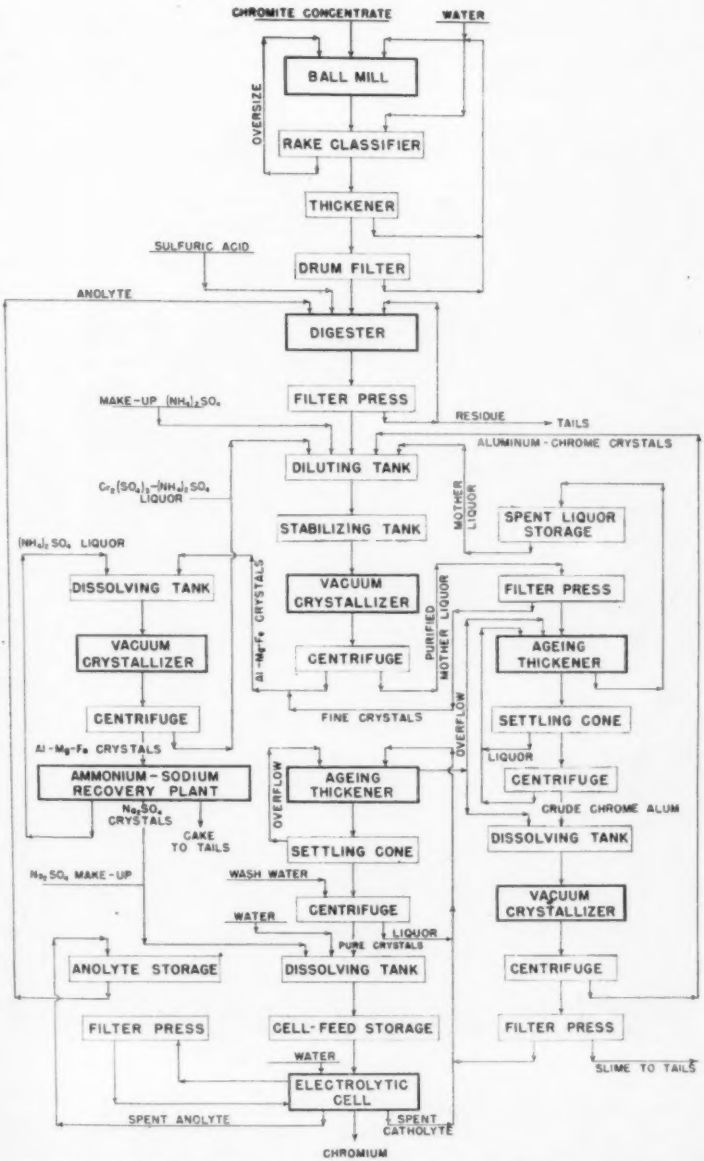

FIG. 1. Equipment flow sheet of electrolytic-chromium pilot plant

mill, 30 in. in diameter by 46 in. long (76 cm. x 117 cm.), in closed circuit with a 2 ft. x 21 ft. (50 cm. x 6.4 m.) simplex classifier. The overflow from the classifier flows to a 14-ft. (4.3-m.) thickener. The thickener underflow is filtered on a drum filter, and the wet cake stored in a steel tank. Wet

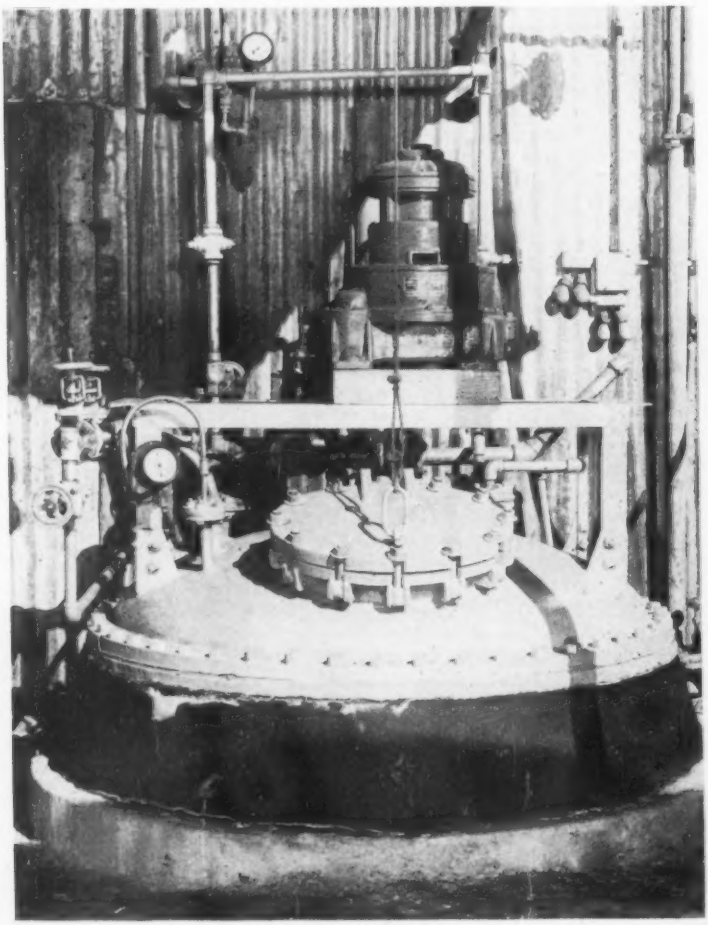

FIG. 2. Top view of digester

filter cake is removed in 500-lb. (227-kg.) batches and digested in a digester lined with sheet lead and brick, using commercial 66° Bé (93 per cent) sulfuric acid and cell anolyte; this reaction is exothermic. The digester, shown in Fig. 2, operates on a 24 hour cycle, and the finished digest liquor is

filtered hot through Saran cloth in an 18-in. (46-cm.) square antimonial-lead filter press and diluted with recycled ammonium sulfate-bearing liquors to a concentration of about 40 g./l. chromium.

The diluted liquor, heated to 80°C. to stabilize the chromium in the green modification, is cooled to 3°C. in a 30-in. (76-cm.) diameter rubber-lined vacuum crystallizer, either in 160-gal. (606-l.) batches or at a continuous rate of 50 gal./hr. (189 l./hr.). A view of the crystallizer floor is shown in Fig. 3. The Al, Mg, and Fe crystallize as ammonium sulfate complexes, along with Glaubers salt, and the mixed crystals are separated from the purified mother liquor in rubber-lined 20-in. (51-cm.) basket centrifuges, Fig. 4. The liquor is clarified further in a 30-in. (76-cm.) wood filter press and sent to a 5,000-gal. (18.9 $m.^3$) Koroseal-lined thickener for crystallization and precipitation of crude chrome alum, which occurs when the chro-

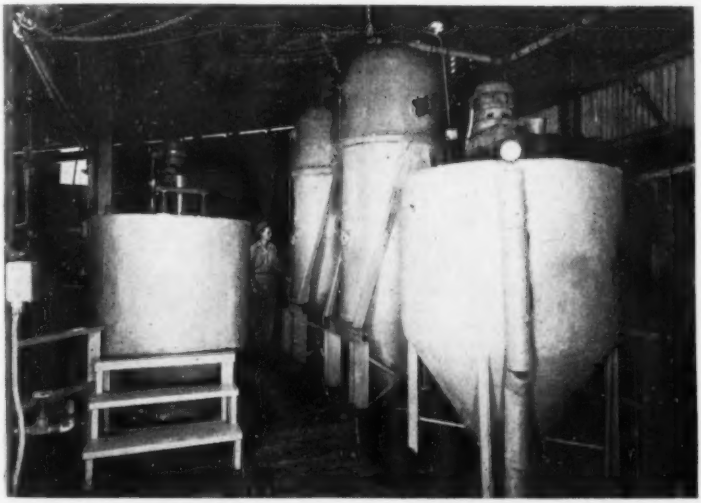

FIG. 3. View of crystallizer floor showing crystallizers and two crystal settling tanks

mium converts to the violet modification. Crude alum is separated from the mother liquor in a basket centrifuge and dissolved in recycled liquor and spent catholyte from the cell at 85°C. At this temperature most of the chromium is again converted to the green modification, but enough remains in the violet modification to coprecipitate with the remaining aluminum when the solution is cooled to 5°C. in a vacuum crystallizer. The aluminum-chromium crystals are returned to the system and the liquor is again clarified and sent to a 2,000-gal. (7,500-l.) thickener for precipitation of pure chrome alum. Pure alum is dissolved in a small quantity of water, along with recovered Glaubers salt, in a 500-gal. (1,900-l.) lead- and brick-lined tank with a Karbate heat exchanger. Cell feed is stored in a 1,000-gal. (3,800-l.) tank at 60°C. and fed continuously from this tank to the pilot cell, using a bucket-type feeder with stainless steel buckets.

The pilot cell (2) contains 5 cathodes, each with 10 sq. ft. (92.9 dm.^{2}) of submerged surface and 10 cast lead-1 per cent silver anodes. The anode and cathode frames are constructed of Lucite, and the diaphragms are of Vinyon. The cell catholyte is circulated at a slow rate through a 12-in.

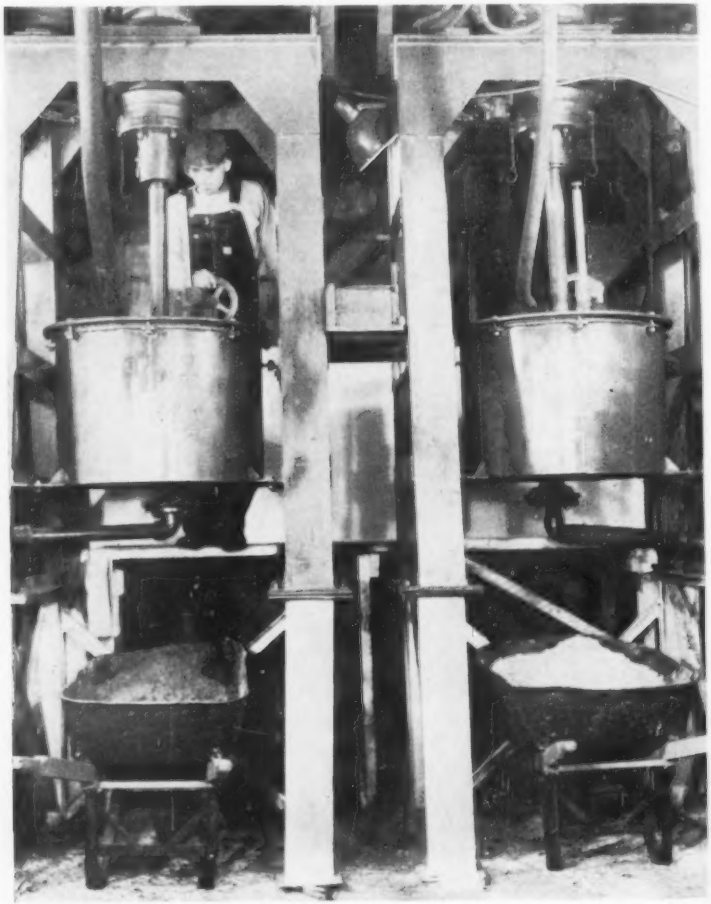

FIG. 4. Two of four basket centrifuges. The dark crystals are chrome alum, and the light crystals are combined Al-Mg-Fe ammonium sulfate complexes.

(30-cm.) Neoprene-covered filter press to remove suspended particles, which cause pits in the deposited metal. Spent catholyte and spent anolyte are both removed continuously by overflowing their respective weirs. Anolyte goes to storage from which it is periodically withdrawn for digestion of

new ore and the spent catholyte, containing divalent chromium, is utilized to reduce iron in the crude chrome alum. The cathode plates are removed at 48-hr. intervals, washed, and stripped by hitting with a rawhide mallet. The stripped plates are straightened, if necessary, washed in hot water and, just prior to reuse, they are dipped in a hot solution of a wetting agent and washed with cold water. They enter the cell wet. Periodically they are cleaned of accumulated chromic oxide by immersion in a hot dichromate cleaning solution and are sandblasted to roughen the surface.

The Fe, Al, and Mg crystals removed by the first crystallization step also contain chromium, ammonium, and sodium sulfates which must be recovered. The chromium is recovered by dissolving the crystals in liquor from the ammonium sulfate recovery circuit and recrystallizing at 3°C. in a 30-in. (76-cm.) diameter vacuum crystallizer. The crystals are cen-

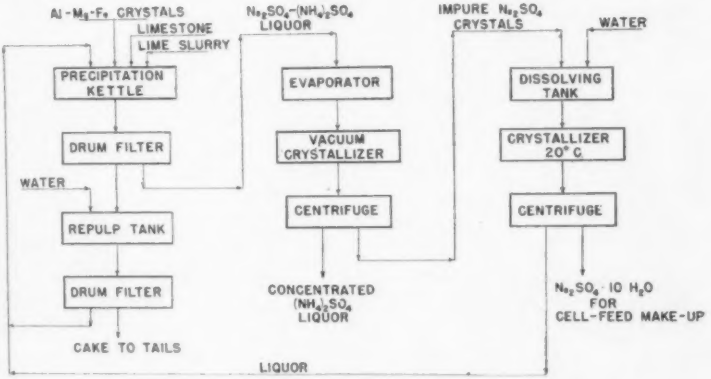

FIG. 5. Detailed flow sheet of ammonium sulfate-sodium sulfate recovery plant

trifuged and go to the ammonium-sodium recovery plant, and the chromium sulfate-ammonium sulfate liquor is returned to the system.

A detailed equipment flow sheet of the ammonium-sodium recovery plant is shown in Fig. 5. The chromium-free crystals are first mixed with return wash water and neutralized to a pH of 5.0 with pulverized limestone in an open tank, and the slurry is then pumped into a closed reaction kettle containing a lime slurry. An ammonia pressure of less than 1 lb./sq. in. develops. When the reaction is complete the slurry is filtered on a 3-ft. x 6-ft. (91-cm. x 183-cm.) drum filter, Fig. 6. The cake is washed by repulping twice and refiltering. The strong liquor is concentrated further by evaporation using a lead coil in an open tank, and a crude Glaubers salt is removed by cooling to 3°C. in a vacuum crystallizer. This salt is purified by recrystallization at 20°C. and used to prepare cell feed. The ammonium sulfate liquor returns to the leaching system.

All tanks in the plant are lined with Koroseal or lead and brick; all centrifugal pumps are made of Worthite. Heat exchangers are made of lead, or Karbate, depending on their location in the flow sheet. Piping is rubber-

lined steel, Saran, or type 316 stainless steel. Lead must be avoided in the flow sheet beyond the precipitation of crude chrome alum, but it is used for most of the equipment in the first part of the circuit. Rubber is unsatisfactory for chromium solutions that are either oxidizing or reducing.

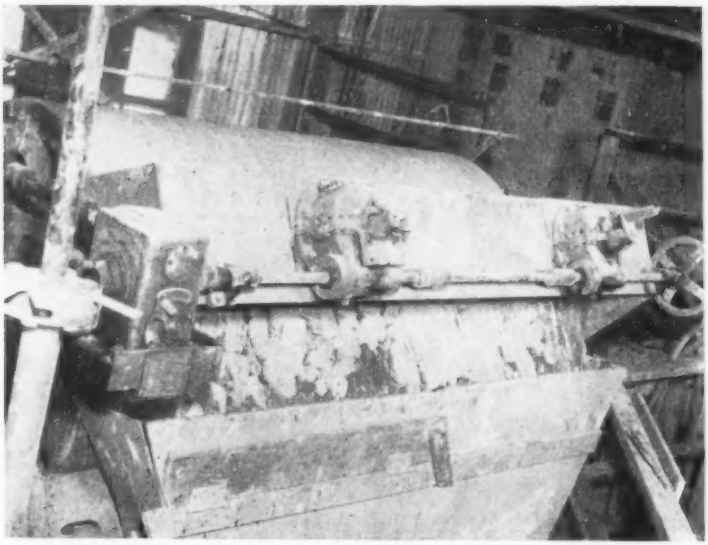

FIG. 6. Drum filter removing combined Al-Mg-Fe hydroxide cake from $(NH_4)_2SO_4$ solution

TABLE I. *Analyses of chromite ore and concentrates*

Source	Cr_2O_3	Fe	Al_2O_3	MgO	SiO_2
Benbow	41.45	17.50	16.40	13.26	3.68
Mouat	39.79	18.17	15.30	14.62	5.63
San Luis Obispo	43.33	10.90	16.18	17.74	5.76

Ore

The chromite used in the pilot plant at present is a lump ore from the San Luis Obispo area in California, but most of the chromite treated has been a gravity concentrate produced by the Anaconda Copper Mining Company for the Office of Metals Reserve, from the Benbow and Mouat (3) deposits located in Montana. All data given in this report are for the Benbow concentrate unless otherwise indicated. Analyses of the various head samples are shown in Table I.

In addition to the major constituents shown in Table I, the ores contain minor quantities of calcium, manganese, and titanium and traces of vanadium, nickel, copper, cobalt, and molybdenum. Nearly all of these metals, as well as lead from commercial acid, must be considered in the purification scheme.

Grinding

Ore must be ground fine to obtain efficient acid utilization in the digester, and the degree of grinding is a function of economic considerations such as grinding costs versus the cost of acid. Of the three ores listed, the San Luis Obispo ore is the most difficult to grind and requires a finer grind to become as reactive as the other ores. The Mouat concentrate is slightly easier to grind than the Benbow and does not need to be ground as fine. All the domestic chromites tested in the pilot-plant required grinding to minus 325-mesh, but satisfactory laboratory tests were made on some softer foreign ores at 200-mesh.

Screen sizing tests were found to be inadequate in determining particle size, and elutriation or settling-rate procedures are used in the plant to determine the point of adequate grinding. The 30-in. x 46-in. (76-cm. x 117-cm.) ball mill grinds 100 lb./hr. (45 kg./hr.) of San Luis Obispo chromite from $\frac{1}{8}$-inch (3.2-mm.) to 70 per cent minus 20 microns and 60 per cent minus 10 microns. The same mill grinds 150 lb. (68 kg.) of Mouat concentrates per hour from 28-mesh. The respective consumption of balls is 14.1 and 10.4 lb. (6.4 and 4.7 kg.) per ton of chromite. It is probable that a higher grinding rate could be obtained with a bowl classifier designed for an overflow of this mesh.

Digestion

The wet filter cake is digested with anolyte from the cell and 66° Bé (93 per cent) sulfuric acid. The mixed acid concentration in the digester is 40 per cent H_2SO_4 with 2.5 to 3 per cent H_2CrO_4. At this concentration, a pressure of 50 to 70 pounds gauge is necessary to maintain the optimum temperature range of 130° to 160°C. If the acid concentration is increased to 65 per cent, digestion will proceed rapidly at atmospheric pressure. However, in the presence of even minor quantities of $(NH_4)_2SO_4$ the acid concentration must be kept at 40 to 45 per cent to prevent the formation of insoluble dehydrated ferric ammonium sulfate (4). Ammonium sulfate is a necessary constituent of the electrowinning bath and cannot be removed from the anolyte. The insoluble ferric ammonium sulfate forms a voluminous precipitate, which usually includes a prohibitive proportion of the chromium.

Chromic acid is necessary to catalyze the digestion reaction, the exact quantity being a function of the sulfuric acid present at the beginning of the digestion reaction and, to a lesser extent, the particle size of the chromite. The optimum ratio of hexavalent chromium to H_2SO_4 is 0.032 per cent, and the chromium concentration of the cell catholyte is controlled to provide this amount or slightly more. An increase above 0.032 per cent of the H_2SO_4 has no appreciable effect but a decrease results in a sharp drop in efficiency. Table II shows the results of 11 consecutive tests

An acid utilization of over 100 per cent indicates the formation of some basic sulfate. The pH of a digest liquor with balanced sulfate is normally zero, because of hydrolysis, so that considerable free acid is actually present. An over-all acid utilization of about 98 per cent and a chromium recovery of 99 per cent is obtained by charging 10 per cent extra ore to each of 10 digests and then digesting the combined residues in the eleventh batch. The residue reacts more readily than the original ore.

All of the constituents of the ore are dissolved with the exception of the silica but some silica is always present in the plant liquors. The digest liquor also contains a small quantity of chromic acid that is not reduced by oxidation of ferrous iron, but which is destroyed by adding about 3 pounds of shredded newspaper to the digester before filtering.

Crystallization of iron, aluminum, and magnesium

Trivalent chromium salts form several distinct kinds of solutions (5) but for the present process only three kinds need be considered; first, the violet or alum-forming modification; second, the green modification, or modifications, which does not form alum; and third, hydrolyzed forms of the green modification (or possibly of both the violet and green modifications). At equilibrium, the relative quantity of the violet and green is determined by the temperature, shifting toward the green with a rise in temperature and toward the violet with a drop in temperature. This shift is extremely slow, particularly toward the violet, but is increased greatly by the alum-forming salts K_2SO_4 and $(NH_4)_2SO_4$. Hydrolysis is produced by heating or by addition of a strong base to a hot solution. Hydrolyzed solutions revert slowly in the presence of free acid but, as determined by the present investigations, the reversion is rapid in the presence of the divalent chromous ion.

TABLE II. *Effect of hexavalent chromium concentration on efficiency of acid utilization*

No. of tests	Cr^{6+}/H_2SO_4	Acid utilization
		%
7	0.0317	101.0
4	0.0298	93.6

The rate of conversion to the alum-forming violet modification decreases at low temperatures. Thus, while a low temperature shifts the equilibrium point toward the violet, the rate is so slow at temperatures below 15°C. that concentrated plant liquors can be stored, centrifuged, and clarified without losing chromium.

If the diluted digest liquor, containing an excess of ammonium sulfate, is heated to 100°C. for several hours or is strongly hydrolyzed by adding a strong base, such as anhydrous NH_3 or Na_2CO_3, and is then cooled to 5°C. no chromium alum will be precipitated. Unfortunately, however, this treatment also prevents effective precipitation of ferric iron and produces magnesium ammonium sulfate crystals so fine that they cannot be separated by centrifuging. From existing solubility data, phase rule and solubility studies, and empirical crystallization tests in a vacuum crystallizer, it has been determined that the most useful separation of iron, aluminum, and magnesium from chromium can be obtained by heating the liquor for several hours at 60°C. and then for 1 hour at 80°C. immediately before cooling for crystallization. Fig. 7 shows the effect of prolonged heating at 60°C. on the solubility of iron and magnesium in the liquor and the loss of chromium in the crystals at 5°C. In all cases the solutions were heated for 1 hour at 80°C. and the final chromium concentration of the liquor was 50 to 52 g./l. It will be noted that the optimum time for chromium and magnesium is 5

hours, with a chromium loss of 0.9 per cent. The magnesium concentration in the purified mother liquor is more critical than the iron, as the crude chrome alum must be free of magnesium, and the temperature solubility curve for magnesium-ammonium sulfate is relatively flat. In the plant, it is impossible to treat all of the liquor for the optimum time so the actual chromium loss in the crystals is higher than 0.9 per cent.

With other variables constant, the loss of chromium in the crystals is directly proportional to the chromium concentration of the liquor in equilibrium with the crystals, and above 52 g./l. this loss becomes too high for subsequent efficient recovery. An original chromium concentration

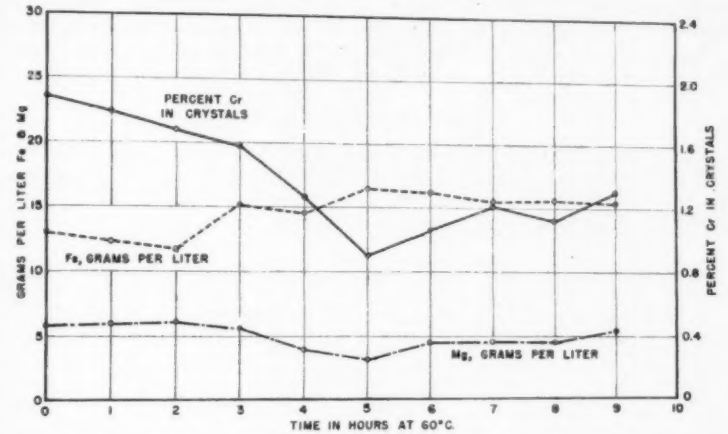

FIG. 7. Effect of prolonged heating at 60°C. on solubility of iron and magnesium in the liquor and chromium content of crystals at 5°C.

TABLE III. *Composition of liquor and crystals produced in primary crystallization step*

	Cr	Fe	Al	Mg	NH_3	Na
Liquor, g./l.	52.0	12.8	0.04	1.4	53.6	48.0
Crystals, %	1.13	2.83	1.23	1.16	3.63	3.24

of 39.3 g./l. gives a final concentration of 52 g./l., as water is lost in the crystals and by evaporation in the vacuum crystallizer. Table III shows the average liquor and crystal compositions for 30 days of continuous operation. The crystals consist of Glaubers salts, magnesium-ammonium sulfate, and various coprecipitated alums of ferric iron, aluminum, and chromium. If ferrous iron is present, ferrous magnesium ammonium sulfate also precipitates. Seeding is necessary for the Glaubers salts but has no apparent effect on the remaining crystals.

The pH of the diluted digest liquor should be between 0.6 and 0.9. A higher pH results in a purified mother liquor which will not readily yield

chrome alum when aged, and also increases the iron solubility. A lower pH results in the formation of insoluble ferric ammonium sulfate of approximately the same type as previously described. A balanced solution, with respect to sulfate and cations, will have a pH of about 0.7 at this point in the flow sheet. If nearly all of the acid is not consumed in the digester, the pH must be raised to 0.6 with NH_3 gas, but this causes hydrolysis resulting in subsequent inefficient removal of magnesium and slow precipitation of chromium in the aging thickener. Fairly complete utilization of the acid in the digester is therefore desirable from the standpoint of subsequent processing as well as acid consumption.

All of the manganese and most of the calcium, titanium, copper, and nickel which accumulate in the mother liquor eventually leave the system in the Al-Mg-Fe crystals. The vanadium distribution between crystals and liquor has not been accurately determined to date.

Chrome alum crystallization

When the purified mother liquor is allowed to age at less than 60°C., the stabilization reactions revert and ammonium chrome alum precipitates. The rate of precipitation depends upon many factors, the principal ones being: the degree of hydrolysis of the original liquor; presence of colloidal

TABLE IV. *Effect of concentration on rate of chromium precipitation as chrome alum*

Concentration of Cr	Time	Crystals produced	Cr depletion
g./l.	*days*	*lb.*	*g./l./day*
34.4	5	5,820	2.85
29.8	14	16,280	2.87
24.1	9	6,650	1.85

impurities; temperature; pH; and presence of chromous ion or SO_2. It is quite possible to produce a chromic ammonium sulfate solution in which the rate of conversion to the violet is so slow that it cannot be determined.

Other factors being equal, the most rapid chromium depletion is obtained by alternately heating the solution to about 35°C. to speed the rate of reaction, and then cooling to 15°C. to precipitate the chrome alum. Such alternate heating and cooling is expensive, however, and a fair rate has been obtained by holding the aging tank at 30°C.

The pH is maintained below 1.2, usually at 0.9, to help reverse the hydrolysis reaction. If the original diluted digest liquor is not hydrolyzed too strongly by either heating above 80°C. or by adding NH_3, the pH will not increase to the point where control is necessary. A strongly hydrolyzed solution reverts very slowly and the degree of hydrolysis is more important to proper aging than conversion from the green to violet modification. A pH rise from incoming to stripped liquor of more than 0.2 indicates excessive hydrolysis.

The aging thickener overflow is kept at 30 g./l. of chromium so that the incoming solution is depleted from 52 to 30 g./l. Allowing for volume changes, 48.6 per cent of the chromium is recovered as crude chrome alum and 51.4 per cent is recycled. It would be desirable to obtain a greater depletion, but a much larger aging tank would be necessary. Table IV

shows the relationship between concentration and rate of depletion. A sharp drop always occurs below 29 g./l.

The magnesium-free liquor from the chrome alum purification circuit is returned to the aging thickener even though no chromium is stripped from this liquor. It helps to dilute the aging liquor, to make up for water lost with the crystals and by evaporation, and prevents saturation of the magnesium. Table V shows that the incoming and outgoing liquor differ appreciably only in chromium content. While the magnesium increases slightly, the ammonium sulfate decreases causing a corresponding increase in magnesium solubility. The crude alum contains 9.8% Cr, 0.78% Fe, 0.05% Al, 0.10% Na, and sufficient lead, nickel, molybdenum, copper, and cobalt to make further purification necessary. It contains less than 0.001% magnesium and not enough calcium, titanium, vanadium, or manganese to cause trouble in the electrodeposition step.

Purification of crude alum

It will be noted that the crystals contain about three times as much aluminum as removed from the liquor. This phenomenon is caused by carry over of siliceous slime which does not show in the liquor analysis. The siliceous slime contains aluminum, magnesium, and ferrous iron and

TABLE V. *Analyses of spent mother liquor compared with incoming liquor, g./l.*

Liquor	Cr	Fe	Al	Mg	NH_3	Na
Incoming	52.0	12.8	0.04	1.41	53.6	48.0
Spent	30.0	12.6	0.01	1.46	51.9	52.8

probably is partly digested ore. When the crystals are dissolved at 85°C., the aluminum goes into solution but the magnesium is released only under the effect of the electrolytic cell. The aluminum, therefore, is removed by crystallization and the magnesium, lead, nickel, molybdenum, copper, and cobalt by careful clarification of the cold liquor. The aluminum can be removed effectively only by coprecipitation with chromium; about 8 per cent of the chromium is removed with the aluminum and recycled. Most of the aluminum can be filtered out of the purified mother liquor, but that remaining in solution precipitates more completely than the chromium, making crystals which still contain more aluminum than can be tolerated in the cell. The volume of the liquor at this point is only 32 per cent of the volume of the purified mother liquor.

The presence of siliceous slime in the crude chrome alum is essential to successful removal of the heavy metals, and the silica analysis of the cell feed is a better indication of solution purity than analysis of the individual metals. Successful removal is used here to indicate removal below the quantity that is deleterious to cell operation.

Iron is lowered to 0.03 per cent by reducing the ferric iron in solution with spent catholyte which contains divalent chromium, and recrystallizing in a second thickener. If the recrystallization step is omitted, the cathode deposit contains 7 to 8 per cent Fe but is satisfactory in every other respect. The chromium-iron deposit may be preferable for the production of stain-

less steel and other ferrous alloys. If iron-free chromium is desired, the alum is recrystallized twice. A much smaller thickener is required for recrystallization than for the primary crystallization because of the catalytic effect of divalent chromium.

Electrolysis

Cell feed is prepared from pure chrome alum and recovered $Na_2SO_4 \cdot 10H_2O$. It is made by dissolving the crystals at 85°C. and is stored at 60°C. to prevent alum precipitation. Hydrolysis is unimportant because the strongly divalent catholyte causes a rapid reversal of the hydrolysis reaction. The pH of the cell feed is 0.2 to 0.4. Table VI shows the analysis of the feed together with the maximum permissible concentration of impurities.

Increased purity of solutions and studies on the use of higher operating temperatures have increased the current efficiency of the electrolytic cells

TABLE VI. *Analyses of cell feed and permissible concentration of impurities*

Component	Concentration	Permissible concentration
	g./l.	g./l.
Cr	90.5	
NH_3	29.5	
Na	16.9	
Fe	0.3	
Al	0.030	0.125
Mg	0.080*	0.100
Pb	0.001	0.002
Ni	0.001	0.004
Ti	0.003	Not critical
Mo	<0.0005	Not determined
Mn	Trace	Npt critical
Co	Nil	Not determined
Cu	Nil	Not determined
SiO_2	Nil	Not determined

* Mg enters the cell feed with recovered sodium sulfate.

from 45 to 60 per cent since publication of the previous report (1). The sulfur and oxygen content of the metal have also been decreased to a fraction of their former values. The metal now being deposited contains 98.8% Cr, 0.4% Fe, 0.01% S, 0.03% H_2, and 0.17% O_2. It contains practically no acid-insoluble residue as plated, but if heated in vacuum to 800°C. for determination of oxygen by the method of Adcock (6), 0.53 per cent acid insoluble results. This would be equivalent to 0.17 per cent O_2. The metal was previously reported to contain 0.07 S (1) and 0.54 O_2 (7). If the chromium is heated to 450°C. for dehydrogenation (8) water is also driven off and the total chromium analysis is increased to 99.3 per cent, or the total chromium plus iron to 99.7 per cent.

The relationship between catholyte temperature and current efficiency is shown in Fig. 8. The percentage of chromium in the divalent state is also shown to indicate the cause of lowered efficiency at 50°C. Higher operating temperatures require an increase in pH and the wide spread

in points at 37° and 40°C. represent tests at slightly different pH. It is believed that a change in cell design would increase the temperature at which the divalent chromium concentration drops below the critical proportion of the total chromium and would permit testing at higher

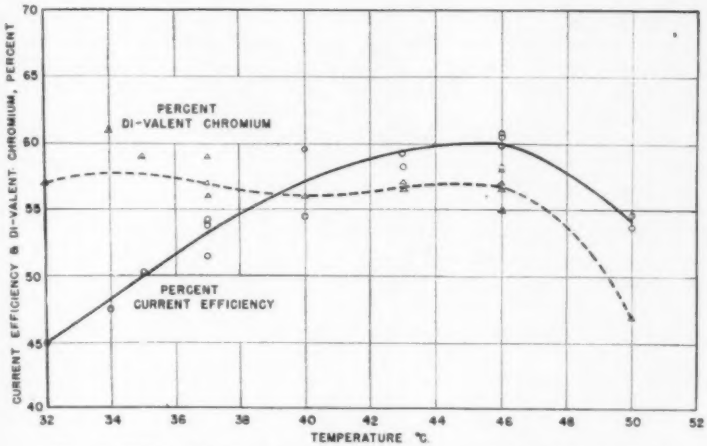

FIG. 8. Effect of electrolyte temperature on current efficiency and stability of divalent chromium

TABLE VII. *Typical cell-operating data*

Cathode area	10 sq. ft. (92.9 dm.²)
Cathode material	Aluminum bronze
Rate of catholyte flow	0.3 gal./sq.ft./min.(0.12 l./dm.²/min.)
Current density	67 amp./sq.ft. (7.3 amp./dm.²)
Cell potential	4.3 volts
Current efficiency	60.6%
Kw.-hr./lb. metal	5.0 (11.0 kw.-hr./Kg.)
pH	2.25
Na_2SO_3 addition	0.0034 g./l./hr.
Goulac addition	0.0015 g./l./hr.
Temperature	46°C.

Electrolyte analyses

	Cr	NH_3	Na
Catholyte	35.0	47.5	25.0
Anolyte	23.7	11.2	7.9

temperatures. A definite drop in efficiency occurs if the chromium in the divalent state is below about 54 per cent.

Typical operating data for the cell are shown in Table VII. The cathode listed is aluminum bronze but cathodes of stainless steel, aluminum, naval brass, Muntz metal, and phosphor bronze are also used.

Recovery of chromium, ammonium, and sodium sulfates from the Al-Mg-Fe crystals

The Al-Mg-Fe crystals from the primary crystallization contain 1.13 per cent chromium, which represents 29 per cent of the chromium extracted from the ore. About 87 per cent of this loss is recovered by recrystallization.

Loss of chromium in the recrystallized crystals, as would be anticipated, is a function of the concentration of the liquor in equilibrium with the crystals, so it would be desirable to recrystallize in a dilute chromium liquor. Excess dilution, however, returns a large proportion of the iron and magnesium to the system and makes sodium recovery practically impossible. The upper limit of concentration is determined not only by chromium loss but also by the crystal-liquor magma that can be handled in a vacuum crystallizer. A fair balance is obtained at 20 g./l. chromium, and the plant is operated to give about this concentration. Table VIII shows the average crystal and liquor analyses for 30 days' operation. All of the aluminum and magnesium, 99.4 per cent of the iron, and 3.8 per cent of the chromium from the ore leave the system in these crystals. The iron and magnesium in the recycled liquor represent 16 per cent and

TABLE VIII. *Average crystal and liquor analyses, recrystallization of Al-Mg-Fe crystals*

	Cr	Fe	Al	Mg	Na	NH_3
Liquor, g./l.	20.50	9.68	0.04	1.49	46.00	61.40
Crystals, %	0.17	2.76	1.44	1.29	3.84	3.62

6 per cent respectively of the iron and magnesium in the crystals from the primary crystallization.

The recrystallized Al-Mg-Fe crystals are added at hourly intervals in 200-lb. (91-kg.) batches to an open tank containing a small quantity of return wash water and the theoretical quantity of minus 270-mesh limestone to precipitate the iron and aluminum from 1 ton of crystals. Reject liquor from the final $Na_2SO_4 \cdot 10H_2O$ recovery is also added at this point. The water is inadequate to dissolve the crystals at room temperature, but new crystals dissolve as the iron and aluminum are precipitated from solution. After 10 batches have been added, the reaction proceeds for an additional two hours to bring the pH to 5.0. A pH above 5.5 results in loss of NH_3 in an open tank.

The mixture is then pumped into a closed kettle containing an excess of lime slurry. The magnesium sulfate is, thus, neutralized with solution having a high pH, a technique that is essential for obtaining a readily filterable cake. Magnesium precipitation is over 95 per cent complete with 165 per cent of the theoretical lime. Once precipitated, the $Mg(OH)_2$ is so slightly ionized that it does not readily react with $(NH_4)_2SO_4$ to liberate NH_3. The slurry does have an NH_3 vapor pressure, mostly from excess $Ca(OH)_2$, which is proportional to the $(NH_4)_2SO_4$ concentration. At 98 g./l. of $(NH_4)_2SO_4$, equivalent to 25 g./l. NH_3, the loss by vola-

tilization amounts to 5 per cent and an additional 5 per cent is lost in the cake. Theoretical repulping calculations show that the loss in the cake after two repulpings should be less than 3 per cent and it is probable that the wash obtained in the pilot plant can be improved upon. The sodium loss in the cake is also 5 per cent, but because of the large recycled load the loss is nearly 20 per cent of the sodium that would be recovered as $Na_2SO_4 \cdot 10H_2O$. The filter cake from the original filtration and the two repulpings average 40%, 43% and 44.8% solids respectively, and the filtering rate averages 1 lb. of wet cake/ft.²/min. (5 kg./m.²/min.).

The filtrate contains $(NH_4)_2SO_4$, Na_2SO_4, and 0.3 g./l. Mg. It is concentrated to about 40 per cent of its original volume by evaporation and cooled to precipitate $Na_2SO_4 \cdot 10H_2O$. Even at 3°C., the solubility of sodium is 46 g./l. and only 36 per cent of that present is precipitated; the rest must be recycled. The $Na_2SO_4 \cdot 10H_2O$ recovered is contaminated by 0.38 per cent Mg as $(NH_4)_2SO_4 \cdot MgSO_4 \cdot 6H_2O$. The concentrated ammonium liquor is returned to the system, and the wet crystals are dissolved in a small quantity of water, 70 gallons/ton of crystals (292 ml./kg.), and recrystallized by cooling to 20°C. in a vacuum crystallizer.

TABLE IX. *Raw material required for production of electrolytic chromium*

Material	Quantity per ton of Cr metal
	tons
Benbow concentrates (95% Cr Recovery)	3.720
Sulfuric acid (93% Commercial)	5.027
Limestone	3.318
Lime	1.660
Ammonium sulfate	0.325
Sodium sulfate	0.137

A final crystal is obtained which averages 13.5% Na, 0.28% NH_3, and 0.07% Mg.

Only a limited quantity of sodium sulfate has been recovered by the above procedure because of efforts to circumvent the sodium sulfate problem by purifying some of the mother liquor to the point where it can be used directly to provide sodium for cell feed preparation. Some difficulty has been experienced in obtaining an entirely satisfactory electrolyte, but if this procedure can be used several economies will result. The first Al-Mg-Fe crystals will be reduced by 23 per cent in weight and the second crystals by 29 per cent, less lime will be required to precipitate magnesium, less evaporation of $(NH_4)_2SO_4$ liquor will be required, and sodium sulfate losses will be practically nil.

RAW MATERIALS

The quantity of raw material necessary to produce one unit of electrolytic chromium from the Benbow concentrates by this process is shown in Table IX.

SUMMARY

Chromic sulfate liquor prepared by direct dissolution of chromite in sulfuric acid contains major quantities of iron, aluminum, and magnesium;

minor quantities of calcium, titanium, and manganese; and accumulative traces of vanadium, nickel, copper, cobalt, and molybdenum. Most of these metals must be separated from the chromic sulfate to make a suitable electrolyte for electrowinning.

Data obtained from an integrated pilot plant, rated at 70 lb./day (32 kg./day), show the process control necessary to remove the critical impurities, using standard unit processing equipment.

Electrolytic chromium, which compares favorably with metal produced from the conventional chromic acid bath, may be deposited continuously at a current efficiency of 60 per cent from a chromic sulfate electrolyte prepared by the outlined procedure. The metal contains about 0.4 per cent iron, but the iron can be varied from almost nothing to 9 per cent. About 10,000 pounds of metal have been produced.

ACKNOWLEDGMENT

The studies on electrolytic chromium are being carried on at the Boulder City Electrometallurgical Experiment Station, Boulder City, Nevada. This station is directed by C. W. Davis, Chief, Boulder City Branch, Metallurgical Division, and his assistance with the more difficult phases of the problem is gratefully acknowledged. Acknowledgment is also made to E. T. Leidigh, formerly Associate Chemical Engineer, Beveridge Stead, Associate Technologist, and W. R. Benedict, Assistant Technologist, for help with the plant supervision; to P. R. Perry, Chemist, for supervision of routine and special analytical work; to R. W. Lewis, Chemist, for supervision of special spectrographic and spectrophotometric studies on chromic sulfate solutions; and to C. T. Baroch, Senior Metallurgist, for critical review of the manuscript.

Any discussion of this paper will appear in the discussion section of Volume 94 of the Transactions of the Society.

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